Developing suitable polymer semiconducrors for the application in BioFETs

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Chapter 1

Molecular electronics; general introduction

With the need for cleaner, faster and smaller electronics increasing, electronics, Molecular Electronics (ME) – the use of molecular components in electronic devices - has become an important field in chemistry, physics, and material science research in the last few years. This chapter, will give a small overview of the field, starting with a general introduction, followed by a closer look at the design and synthesis of more environmentally stable materials for molecular electronics. This chapter will end with a more detailed description of the main subjects of this thesis.

1.1 Introduction

In modern society we are surrounded by mobile phones, digital music players, digital cameras, flat screen TVs, laptops, and many other electronic gadgets. Almost everybody has them—we are addicted to these products of recent technology. We now take for granted the pace at which smaller, faster versions of these gadgets appear. However, these consumer electronics have not been around that long. The first transistor was invented only 60 years ago in 1947 by William Shockley, John Bardeen, and Walter Brattian at Bell Labs [1] and it was not until the late 50's that complete circuits where incorporated on a single piece of silicon.

Looking at the pace at which these circuits became smaller, Gordon Moore made his famous prediction in 1975 that the density of transistors on chips would double every two years[2]. This prediction is now generally known as Moore's Law and has been revised to the statement that the computation power is doubled every 18 months[3]. Although the law still holds today, fabrication methods for semiconductor chips are reaching their physical limits[4]. Intel has stated that their 193 nm dry lithography process, used since the fabrication of their 90 nm microprocessors in 2003, has reached its limit and they are now developing new lithography techniques like immersion lithography or deep ultraviolet lithography to be able to produce the 22 nm microprocessors in 2011. Whether it is possible to go even smaller (<22 nm) using lithography techniques remains uncertain. If we want to sustain Moore's law, other methods need to be developed to produce electronics on an even smaller scale.

Molecular Electronics (ME) has the potential to go much smaller by using components that consist of just tens or hundreds of molecules. It is therefore not surprising that the field has been growing rapidly over the last 20 years[5]. Molecular Electronics can be divided into two main categories; organic materials (macroscopic) and electronics at the molecular level[6,7,8]. These two categories are strongly connected and cannot be treated separately; A better understanding on the molecular level will translate to improvements on the macroscopic scale. Growing research in both categories has resulted in a increasing knowledge of molecular electronics in general[9]. This progress has led to the first commercial applications of organic solar cells[10] and organic LEDs[11], and more is coming.

1.2 Conjugated polymers

1.2.1 Introduction[12,13,14]

One of the most widely studied classes of materials in the field of molecular electronics is conjugated polymers. These polymers undergo an insulator-metal transition when doped (partially oxidized or reduced). Replacing metals and semiconductors with these conducting polymers can result in all-plastic devices, which can be more flexible, lighter, cheaper, less energy consuming, and easier to make than traditional devices bases on silicon. Polymers are also cheap to manufacture and are in general, good insulators for both heat and electricity. It is therefore somewhat confusing that there are polymers that can be made conducting. The discovery of, and reason for this unique property will be explained below

To understand conductivity in organic materials we have to begin with Molecular Orbital (MO) theory. For a solid with an infinite number of contributing atomic orbitals, MO theory, in combination with the Linear Combination of Atomic Orbitals (LCAO), predicts that instead of discrete energy levels, continuous bands of degenerate orbitals are formed. The energy levels in the bands have negligible energy separation and the movement of electrons between energy levels within a band is facile at room temperature. As with small molecules, the bands are filled with valence electrons, starting with the lower energy valence band.

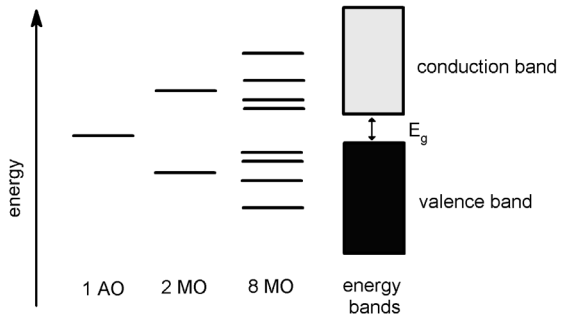


Figure 1.1 Schematic representation of the formation of energy bands in conjugated materials. From left to right; the energy levels diagram of 1, 2 and 8 degenerate molecular orbitals, and a band structure.

Most metals are electron deficient elements, which results in partially filled energy bands of delocalized electrons, and conductivity. Most insulator materials, however, have a completely filled valence band, which localizes electrons. Promoting an electron from the valence band to the conducting band would result in conductivity, but the energy difference (E_g) between the two bands is too large, resulting in a thermally inaccessible transition. In the case of semiconductors, the valence band is also completely filled, but the E_g is smaller

and it is possible to make the material conductive by adding or removing an electron, so called doping.

The delocalization of electrons and the presence of partly filled energy bands are the reasons for the high conductivity of metals. For polymers the situation is different. Although the overlap between atomic orbitals in a polymer chain also causes the formation of energy bands, they are completely filled. In most traditional polymers, valence electrons are bound in sp^3-hybridized covalent bonds leading to a filled energy band and localized electrons (insulator). In conjugated polymers however bonds are formed between sp^2-hybridized or sp hybridized carbons, leaving free electrons in un-hybridized p-orbitals. These unpaired electrons in the lowest occupied anti-bonding π-orbital should lead to a partially-filled valence band, complete delocalization of the electrons over the polymer and, therefore, metallic properties. In reality, conjugated polymers are semi-conductors. This is due to the so-called Peierls instability. Peierls showed[15] that, in 1d metals, via a small lattice rearrangement, atoms can move from equally-distanced to alternating spacing, leading to the formation of atom-pairs. This dimerization produces a more stable structure and a lower energy state for the electrons, resulting in a filled valence band and a relatively small band-gap of ~1.5 eV[16] in polyacetylene.

The above representation is somewhat simplified and one has to remember that predicting whether a material will be conducting, semi-conducting or insulating depends not only on the number of valence electrons, but also on the band structure. The energy range of the bands is different in each solid and the individual bands can have a discrete character, overlap, or 'touch'. In the case of overlapping bands for example, an empty band overlapping with a filled band will result in metallic behavior. This is the case in group 2 metals.

Semi-conducting behavior in organic polymers was first reported by Weiss et al.[17], but that report on highly conductive oxidized polypyrrole black is rarely cited. Rather a collaboration between Shirakawa, MacDairmid and Heeger on the doping of trans-polyacetylene[18,19] is now seen as the beginning of research on conductive polymers and is what they were awarded the Nobel Prize for in 2000.

Shirakawa, MacDairmid, and Heeger suggested that adding or removing of electrons in the backbone of polyacetylene would create mobile charge carriers and lead to an increase of electrical conductivity. They proved this by oxidative doping with iodine, which resulted in an increase in conductivity from 10^{-5} to 10^{3} Scm^{-1} . This doping process is a redox process in which the iodine is reduced and the polymer is oxidized resulting in positive charge carriers that can delocalize over the conjugated polymer backbone. By itself this does not result in

bulk conductivity. Inter-chain hopping is necessary for conductivity in conjugated polymers[20,21].

The doping of inorganic materials results in the removal of an electron from the valence band (p-type doping) or the addition of an electron to the conduction band (n-type doping), leading to partially filled bands. Simply extending this mechanism to organic semiconductors was found to be inaccurate[22,23]. The removal (or addition) of an electron from (or to) a conjugated polymer causes a small lattice distortion[24] in the polymer structure, which results in the formation of discrete energy levels inside the band gap. Increasing the amount of doping results in the formation of bands within the band gap[13]. Depending of the type of polymer and the degree of doping, several charged states can be generated[25] as shown in Figure 1.2 (solitons are only found in trans polyacetylene).

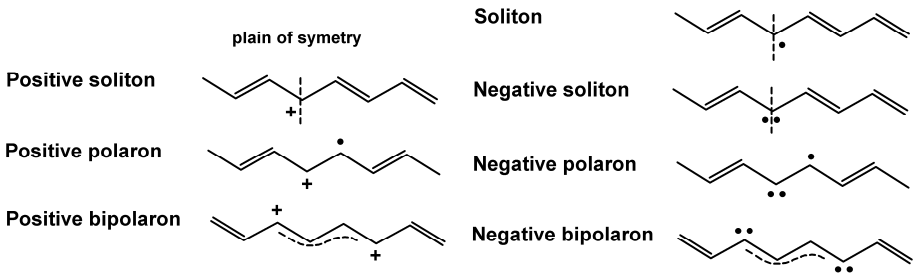


Figure 1.2 Representation of charge carriers on part of a poly(acetylene) chain.

Polarons and bipolarons are known to be the main structures of charge carriers in conductive polymers, but the complete conduction mechanism in not yet fully understood.

Since the discovery of conductivity in polyacetylene, a large variety of conductive polymers have been described in literature. While the first studies on conjugated polymers focused mainly on the properties of homo-polymers like polyphenylenes, polyphenylene vinylenes and polythiophenes, better understanding of these systems has led to the development of more complex polymers. The development of new donor-acceptor type conjugated polymers for example affords control over the electronic properties, as will be discussed in the next paragraph. Examples of some of these polymers can be found in Figure 1.3.

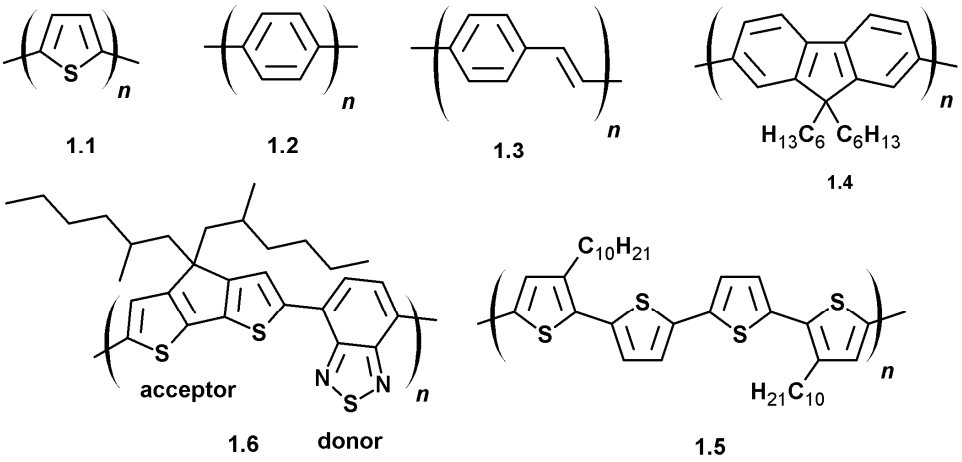


Figure 1.3 Examples of conjugated polymers: 1.1) polythiophene, 1.2) polyphenylene, 1.3) polyphenylene vinylene, 1.4) poly(9,9-dihexylfluorene) 1.5) PCPDTBT 1.6) poly(2,2-decylquarterthiophene). Polymers 1.1, 1.2, 1.4 are homopolymers, 1.6 is a donor-acceptor polymer.

1.2.2 Band gap engineering

As seen in the previous section, the electronic properties of conjugated polymers are closely related to the electronic levels of the polymer. Controlling the absolute position of the energy bands and the size of the band gap is therefore very important in the design and synthesis of conjugated polymers.

There are several ways to influence the band gap (E_g) of a conjugated polymer. The E_g value is a combination of bond length alternation Δr ($E_{\Delta r}$), the resonance energy stabilization (E_{res}), the inter-ring torsion angle (E_{Θ}), substituents effects (E_{sub}), molecular weight of the polymer (E_{mw}) and the intermolecular interactions (E_{int})[12,26,27].

As was shown, the band structure of a conjugated polymer originated from the orbital overlap between individual monomers, going from discrete energy levels with large energy separation to energy bands with negligible energy separation. Thus, increasing the degree of polymerization decreases the band gap.

The alternating structure of single and double bonds found in conjugated polymers, originates from the Peierls distortion and contributes to the formation of a band gap. Therefore, the bigger the bond-length alternation, the larger the band gap.

For polymers that can adopt both aromatic and quinoid resonance forms, like polythiophenes, the energy of these forms is not equal[13,27,26].

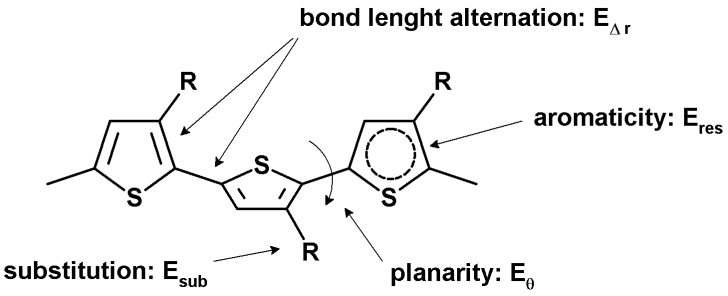


Figure 1.4 Schematic representation of the structural factors that influence the band gap.

In most cases the aromatic form is more stable because of the resonance energy gained. These polymers will have a larger band gap than those with a more dominant quinoid character.

In a conjugated ring system, the inter-ring torsion angles determine, to a large extent, the delocalization of the π-electrons along the polymer backbone. The band gap increases from a coplanar (0 °C) to a perpendicular (90 °) configuration[28]. Brédas et al. stated that in order to have good π-overlap and thus a conducting band structure, the π-orbitals must be within 30° of co-planarity[29]. The torsion angles in aromatic ring systems are greatly affected by the steric hindrance between atoms or groups attached to the rings. The position of substituents on a polymer backbone can therefore influence the torsion angle, and thus the band gap. The development of fused ladder polymers resulted in polymers with rigid structures and small band gaps, but most of these polymers suffer from solubility problems, limiting the practical use[30].

Besides affecting the torsion angle, substituents can directly influence the band gap. Substituents tend to affect occupied orbitals more than unoccupied, thus electron donating substituents like alkyl tails, alkoxy- and alkylsulfonyl groups tent to decrease the band gap by raising the HOMO level while leaving the LUMO level relatively unchanged. Electron withdrawing substituents like carbonyls, halogens, nitro or cyano groups tend to increase the band gap by lowering the HOMO level slightly more than the LUMO level. These electronic effects are small though and are usually dominated by the previously discussed effects.

The above–mentioned factors determine the magnitude of the band gap of a single polymer chain, however the interactions between individual molecules play an important role in determining the band gap. This effect can best been seen in poly(alkylthiophenes). Alkylthiophenes have limited symmetry and this causes the formation of different polymers when the alkylthiophenes are coupled in various ways at the 2- and the 5-positions (figure

1.5a). A 2,2`-coupling is given the name head-to-head (HH) coupling, the 2,5`-coupling is known as head-to-tail (HT) coupling and the 5,5`-coupling is called tail-to-tail (TT) coupling. A random polymerization will therefore result in regio-random polymers.

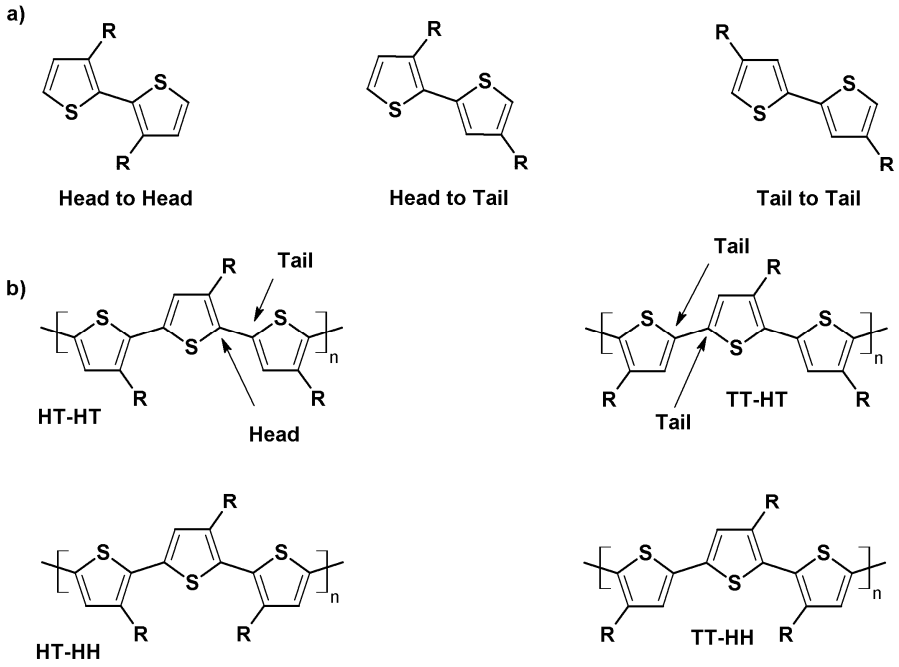


Figure 1.5 Regio-regularity in thiophene chemistry: (a) Denotations for thiophene couplings (b) The four possible oligomeric triads in poly(alkylthiophenes).

These polymers are amorphous and show little mesoscopic ordering. Heeger and Prosa[31] and later McCullough[32] showed that highly regio-regular alkyl substituted polythiophenes form a lamellar structure (interdigitating side-chains) in the condensed phase, resulting in a higher conductivity and a lower band gap then regio-random polythiophenes. The effect of mesoscopic ordering influences the band gap of other polymers as well[33]. (More on this topic in paragraph 1.2.4)

Although the effects on the band gap were discussed separately, they are all strongly connected. This makes it difficult to design conjugated polymers with a specific band gap simply by changing individual parameters. Recently, however, another route has been developed which makes it possible to synthesize conjugated polymers with a specific band gap.

Alternating co-polymerization of strong electron donating and withdrawing monomers results in donor-acceptor polymers with unusually small band gaps compared to the standard

conjugated homo-polymers. The reason for this small energy gap can be explained by the molecular orbital overlap; when the HOMO levels of the donor and the LUMO levels of the acceptor are close in energy, the resulting band structure will have a small band gap. Therefore, the band gap can be altered by changing the combination of monomers, but the previously-mentioned effects still apply for these polymers and need to be taking into account.

Up to now one of the major goals in ME was to synthesize conjugated polymers with a band gap below 1.5 eV. Conjugated polymers are semi-conductors and need to be doped (generation of free charge carriers) to become conductive. The mobility of the charge carriers greatly depends on effective hopping between the individual chains. Under ambient conditions thermally induced hopping is more pronounced in small band gap polymers, leading to a higher mobility. The expected[34] high mobilities and absorption in the visible spectrum would make them good candidates for all kind of applications, such as solar cells, field effect transistor (FETs) and light emitting diodes (LEDs). There is, however, also an increasing interest in the synthesis of polymers with moderate mobilities, but good environmental stability. The next chapter will go into this in more detail.

1.2.3 Stability of conducting polymers

Moving from fundamental research towards application-driven research, it became clear that in addition to good charge transport properties, the environmental stability of conjugated polymers is also very important. The lifetime and performance of a device dependends on the lifetime and degradation pathway of the material[35]. Polymers can react just like other molecular materials if the reactants are made available at reaction sites. There are many external causes of degradation of a polymer such as light, heat, mechanical stress, oxygen, ozone, moisture, atmospheric pollutants, etc[36, 37]. The stability of a conjugated polymer can be discussed in terms of chemical reactivity and/or electrochemical stability. Chemical stability is different for each type of polymer and will therefore not be discussed. Rather, this paragraph will focus on the properties a conjugated polymer must have to be electrochemically stable.

For most devices in ME it is important that the doping of the polymer is controlled and in the 'off-state' of the device doping of the polymer does not occur. Water and oxygen are the main reactive compounds in air[38] and the understanding of their redox reactions with conjugated polymers is important. For a better understanding it is noted that a polymer which can donate an electron is called a p-type polymer (reducing) and a polymer which

accepts electrons is an n-type polymer (oxidizing). In this thesis only p-type polymers are described and the stability of these type of polymers will be discussed.

De Leeuw et al.[38] showed that there are five main reactions concerning water and oxygen and that the stability towards these reactions can be calculated using their redox potentials. The two most important half reactions concerning doping of p-type polymers are giving in Table 1-1.

Table 1-1 The two main half reactions concerning doping of p-type polymers

No.	Reaction	$E_{pH=7}$ (V vs. SCE)
1	$O_2 + 4H^+ + 4e^- \leftrightarrows 2H_2O$ $O_2 + 2H_2O + 4e^- \leftrightarrows 4OH^-$	0.571
2.	$2H^+ + 2e^- \leftrightarrows H_2$ $2H_2O + 2e^- \leftrightarrows H_2 + 2OH^-$	-0.658
3.	$2Pol^0 + 2e^- \leftrightarrows 2Pol^-$ $2Pol^+ + 2e^- \leftrightarrows 2Pol^0$	

Depending on the redox potential of the half-reaction the overall reactions will occur in the direction of reduction or in the direction of oxidation. When the redox potential of the polymer half reaction is higher than that of the oxygen and water, the reaction will occur in the direction of reduction, but when the redox potential is lower it will occur in the direction of oxidation. Simplified, this would mean that, if we only look at the reactions concerning H_2O and O_2, an n-type doped polymer or neutral p-type polymer will be stable towards oxidation by water at redox potentials higher than -0.658 eV (SCE) and stable towards oxidation by water and oxygen at a redox potential higher than +0.571 eV.

In reality extra activation energy is needed for a reaction to proceed and therefore a higher potential is needed. This extra potential is called overpotential and the value depends on the system used. This overpotential means that, in general, n-type doped polymers or neutral p-type polymers are stable to oxidation at redox potentials higher than +0.5 eV (SCE). For the design of conjugated polymers it is important to translate these redox potentials to concrete energy levels of the conjugated polymer. The energy needed to remove an electron from the HOMO level of a polymer to the vacuum is called ionization potential (IP) and correlates with the oxidation of the polymer. The IP can be roughly estimated by adding 4.4 eV to the redox potential obtained (SCE)[39]. The IP of p-type polymer should therefore be larger than 4.9 eV to prevent oxidation by oxygen and water. The energy released when an electron is moved from the vacuum to the LUMO level is called the electron affinity (EA) and correlates with the reduction redox process. The EA is approximately equal to the potential at which the polymer is reduced (vs. SCE) plus 4.4 eV.

Controlling the position of the IP is therefore very important when designing p-type polymers with increased electrochemical stabilities. And although it is possible, by altering

substituents, to control the position of the IP level it is more convenient to increase the band gap which (in general) increases the IP. This concept was proven by McCulloch et al. who showed[40] that, under ambient conditions, going from regio-regular poly(3-hexylthiophene) **1.7** with an IP of 4.8 eV to poly(3,3''-dioctylterthiophene) **1.8** with a IP of 5.4 eV resulted in a increase of three orders of magnitude in on/off ratio taken the polymer was applied in a field effect transistor. Similar effects where found by Fréchet et al.[41] who synthesized poly(dodecylthiophene-3-carboxylate-co-thiophene) **1.9**. The electron withdrawing carbonyl group resulted into a lower lying homo level and an IP of 5.68 eV. The higher IP resulted in more stable polymer which retained its functionality after four months of exposure to air. This is a big increase compared to **1.7** of which the on/off-ratio dropped from 10^3 to 10 within a week.

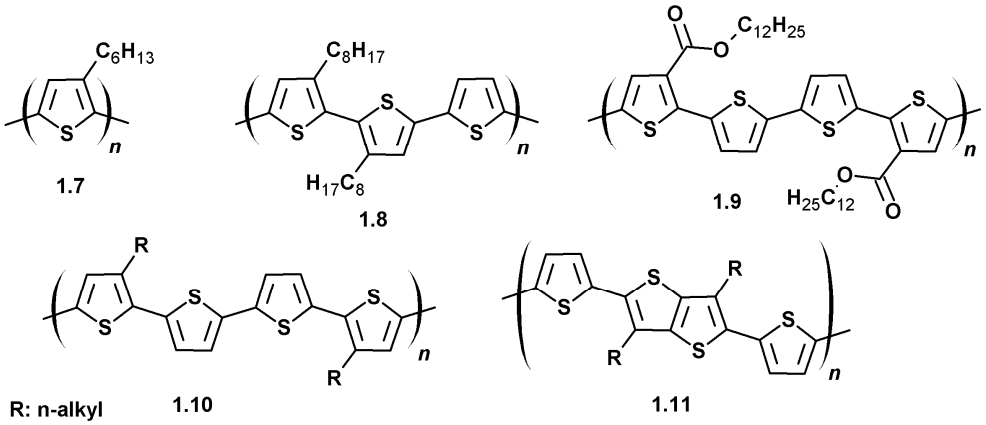


Figure 1.6 Structure of some (stable) polymers as presented in literature. 1.7 poly(3-hexylthiophene) (P3HT), 1.8 poly(3,3-dioctyltertthiophene) 1.9 poly(didodecyl 2,2'-bithiophene-4,4'-dicarboxylate-co-2,2'-bithiophene) 1.10 poly(dialkylquarterthiophene) 1.11 poly(2,5-bis(2-thienyl)-3,6-dialkylthieno[3,2-b]thiophene).

A better understanding of the process of auto-doping has led to the development of new polymers with increased stability and high mobillities, especially in the field of organic thin-film transistors. The traditional P3HT **1.7** is replaced more frequently with more stable polymers like poly(dialkylquarterthiophenes) **1.10** (PQT, IP ~5.1eV) or Poly(2,5-bis(thienyl)-thieno[3,2-b]thiophene)s **1.11** (PTATs, IP ~5.1eV)[33].

1.2.4 The effect of ordering in the film on the device performance

In the previous paragraphs we mainly looked at intramolecular effects on the electronic properties of single polymer chains. In this paragraph we will look at intermolecular effects between polymer chains on the electrical performance in devices.

Most conjugated polymers can be seen as hairy rigid-rod molecules consisting of a rigid π-conjugated backbone with flexible side chains. It is this structure which is so important for the formation of highly conductive polymer films.

When the polymer has a regular structure with a conformation that is close to planar, the rigid-rod structure will lead to the formation of semicrystalline films of crystalline domains in an amorphous matrix. The crystalline domains are formed due to the π-π interactions between adjacent polymer backbones that self-organize into supramolecular lamellar structures[42,43,44]. This increase in organization allows the charge carriers to migrate not only over the single chain but also between chains, resulting in an increased conductivity. This ordering also leads to highly anisotropic transport; there is good transport along the backbone and through the π-stack, but not in other directions. It is therefore very important to know the size and the orientation of these crystalline domains. Frey et al. showed[45] that in a thin film transistor the preferred orientation of poly(3-hexylthiophene) is with the π-π stacking parallel to the substrate. Similar results where found for others regio regular polymers like poly(dialkylquarterthiophenes), poly(dialkylterthiophenes), poly(2,5-bis(2-thienyl)-3,6-dialkylthieno[3,2-b]thiophene)s, and others[33]. If the distance between the individual chains is large enough, the chains can interdigitate[46] leading to a more dense structure. Because of the highly anisotropic electrical transport it is important to obtain large crystalline domains. This can be achieved by annealing of the film and by slow crystallization.[42,43,44] Polymers which do not have a planar conformation and/or lack order do not form these crystalline domains (amorphous) and in general show a lower conductivity.[47]

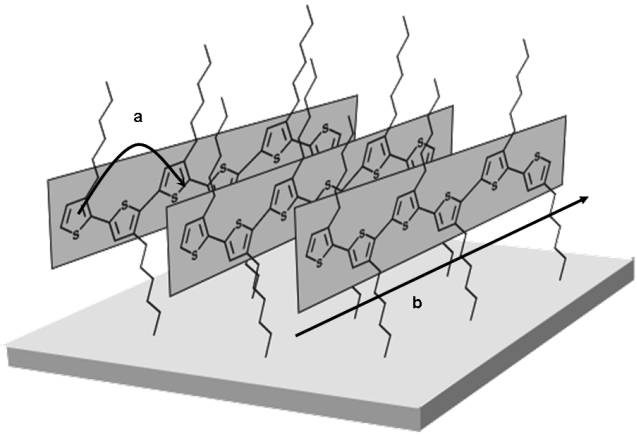


Figure 1.7 Schematic representation of charge-transport in highly regioregular P3HT. a) intermolecular charge transport, b) intramolecular charge transport.

1.3 The synthesis of conjugated polymers

1.3.1 Introduction

As shown in the previous paragraphs the use of poly- and oligothiophene materials is very attractive in ME. By using thiophene based materials it is possible to design devices which are both stable towards oxygen/water and have high mobilities. Throughout the years several synthetic routes have been developed, each with their advantages and disadvantages[48]. The most common coupling routes are either modern organometallic aryl-aryl coupling or electrochemical polymerization. Lemaire et al. have written a detailed and complete review[49] about the aryl-aryl formation and the recent developments in this field. The next paragraphs will give a short introduction of the used coupling reactions in this thesis.

1.3.2 Aryl-aryl bond formation by oxidative coupling reaction

Copper–mediated or catalyzed oxidative coupling reactions are one of the oldest and most extensively used coupling reactions for the synthesis of biaryl molecules, but their use for the synthesis of high molecular weight polymers is limited; the weak oxidation ability of $CuCl_2$ prevents the formation of high molecular weight polymers[50]. Bäuerle et al.[51] could only synthesize dimers and trimers when trying to couple didodecylquarterthiophene by copper–mediated oxidative coupling.

A much better oxidative reagent is $FeCl_3$ and Sugimoto et al. where the first to perform a chemical polymerization of 3-alkylthiophenes using $FeCl_3$ as polymerization agent[52]. The mechanism for the polymerization using $FeCl_3$ is still not completely understood but there is an increasing support for the radical carbocation mechanism[53] as presented in Figure 1.8.

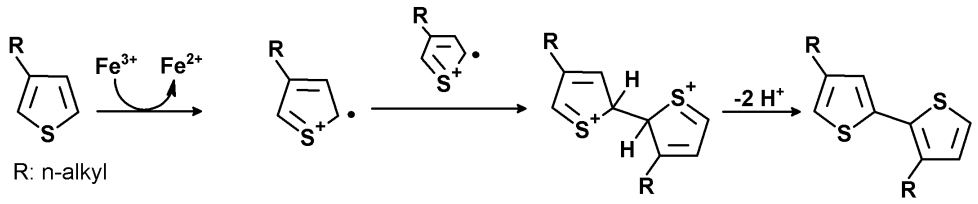


Figure 1.8 Proposed mechanisms for ferric chloride oxidative polymerizations of thiophenes.

The disadvantage of using $FeCl_3$ is that, although it is very reactive, the regio-selectivity is low, which can lead to polymers with a regio-irregular structure[49] and many side-products.
A great example is poly(3-hexylthiophene) (P3HT). The polymerization of the asymmetric monomer 3-hexylthiophene using $FeCl_3$ leads to polymers with four type of linkages, head-to-head (HH), tail-to-tail (TT), head-to-tail (HT) and tail-to-head (TH) couplings. The incorporation of HH linkages leads to twisting of the backbone, a decrease of π-overlap, and poor electronic properties[54] when compared to regio-regular P3HT. Using regio-selective cross-coupling polymerizations (for example McCullough et al.[55] and Rieke et al.[56,57]) results in P3HT with more than 95% HT coupling and polymers with superior electronic properties.

1.3.3 Organometallic cross-coupling polymerization methods

The disadvantages of the oxidative coupling using $FeCl_3$ have led to the development of the more efficient transition metal cross-coupling reactions. In these reactions the formation of C-C bonds is catalyzed by a complex of a low-valent transition metal like nickel or palladium. A schematic representation of the popular coupling reactions can be found in Figure 1.9

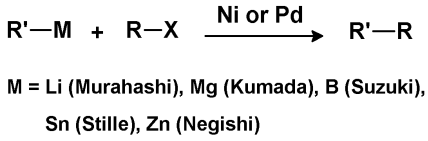


Figure 1.9 Transistion metal catalyzed aryl-aryl coupling reactions.

Kumada coupling

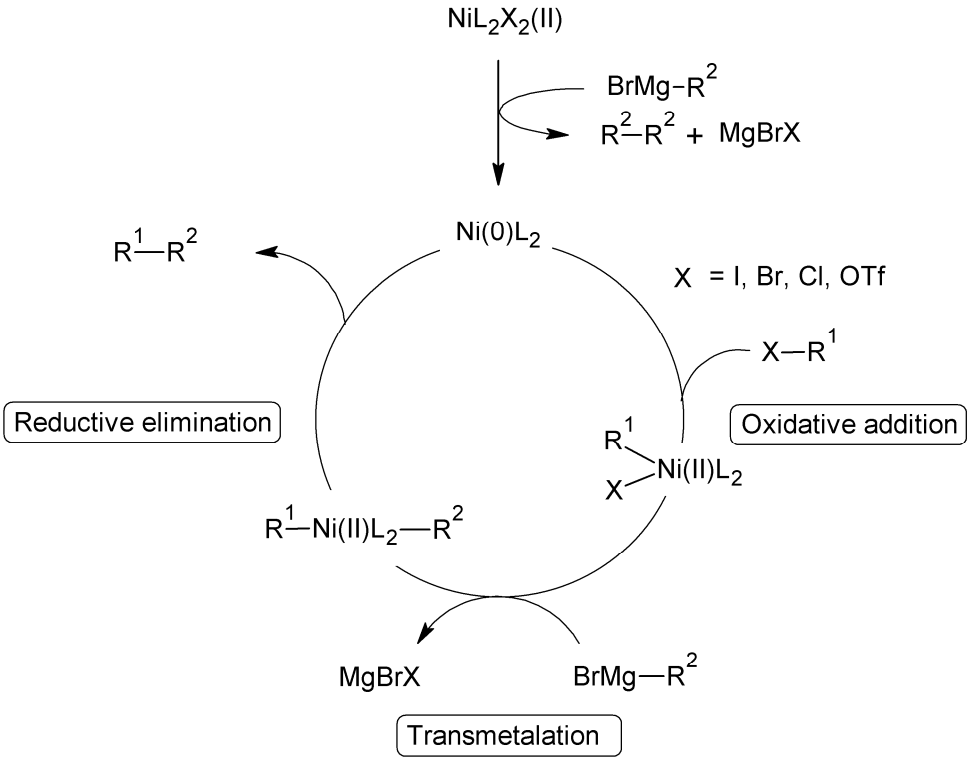


Figure 1.10 Catalytic cycle of Kumada cross-coupling reaction.

One of the first and most common cross-coupling reactions for C-C bond formation is the Kumada coupling. The Kumada coupling allows the rapid coupling between aryl- and vinyl-halides and aryl-, alkenyl- and alkyl- Grignard reagents, catalysed by a nickel (or palladium) complex[49]. Although it is still not completely understood, the proposed[58,59] mechanism of the Kumada coupling is given in Figure 1.10.

To start the catalytic cycle the Ni(II) complex first has to be transformed, *in situ*, to the active Ni(0) complex. During this activation a small amount of Grignard reagent is lost and undesired homo-coupled products are formed. The yield of this homo-coupled side product is low (< 1%) because of the low catalyst loading typical of these reactions. The release of the homo-coupled product from the catalyst complex is promoted by the addition of an organo-halide (RX), oxidizing the Ni(0) complex to the Ni(II) complex: this is called oxidative addition. The next step, in the cycle is the transmetalation step in which the R^2 exchanges Mg for Ni. This mechanism is not well understood, but it is found to be the rate determining step. In the final step the cross-coupled product is eliminated from the complex via reductive elimination, leading to the active Ni(0), and completing the catalytic cycle.

The use of the Kumada coupling to synthesize oligothiophenes via a stepwise procedure is very common, although the reaction can be limited by ineffective magnesium-halogen exchange or ineffective addition of the organic compound to the Grignard reagent. Slow magnesium-halogen exchange occurs in general when the aryl-halide contains more than two aromatic rings, leading to an increase in unwanted side reactions like homo-coupling[60]. McCullough et al. showed that 2-bromo-3-hexyl-5-bromomagnesiumthiophene formed *in situ* could be polymerized using $NiCl_2$(dppp), producing head-to-tail coupled P3HT[55]. NMR showed that the polymers were 93-98% of the desired regio-chemistry.

A mayor drawback of the Kumada coupling is the low tolerance to reactive functional groups, such as amino-, nitrile-, ester- or carbonyl- groups and the sensitivity of the reaction to water.

Stille Coupling

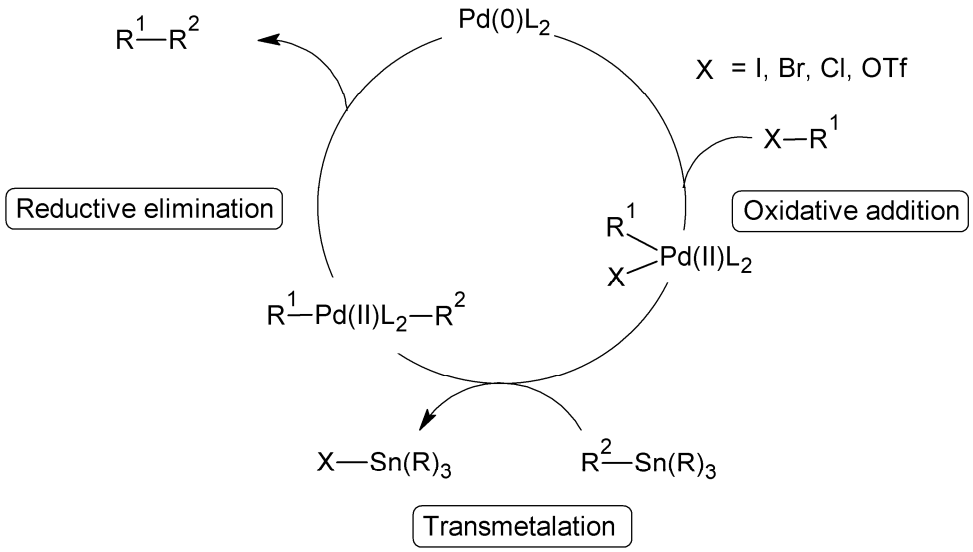


Figure 1.11 Catalytic cycle of Stille cross-coupling reaction.

The Stille coupling has also found widespread use in organic synthesis[49,61]. The Stille coupling is a palladium catalyzed reaction between an organic halide, triflate or carbonyl chloride with a organostannane. For a fast, clean reaction the organic group needs to be of aryl, heterocyclic or vinyl type. The major advantage of the Stille coupling over the Kumada coupling is the growing availability of organostannanes, the high stability towards moisture and air and their compatibility with a variety of functional groups. The catalytic cycle of the Stille coupling is presented in Figure 1.11 and doesn't deviate much from the cycle of the

Kumada coupling. The palladium catalyst can be used as Pd(0) or as Pd(II) complex. There are several mechanisms by which the Pd(II) precursor can be reduced under the reaction conditions used. The complex can be reduced to Pd(0) by two equivalents of the organostannane via a similar process as with the Kumada coupling, leading to undesired homo-coupled product as a side product. The rest of the cycle involves oxidative addition of the organo-halide to the palladium complex, followed by transmetalation of the organostannane compound and reductive elimination of the coupled product to complete the cycle. Although the Stille coupling has been frequently used to produce coupled products in high yields, side-reactions can dominate the reaction[61,62,63]. Homo-coupling of stannanes is one of the most common side reactions in the Stille coupling, even when Pd(0) is used. It is proposed that the homo-coupling is mediated by atmospheric oxygen, therefore extensive degassing is very important. Homo-coupling of the organic electrophile is also observed and the mechanism involves the metal–halogen exchange seen in other transition metal catalyzed cross-coupling reactions. The three alkyl groups on the tin, often methyl or butyl, are supposed to be 'non-transferable' ligands, but it this was found not to be true. The selectivity for the desired coupling is high but at slow reaction rates this side reaction (alkyl shift) can be important.

One of the most commonly used palladium catalyst is Tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) because it is readily available and relatively stable. Unfortunately, it was found that a non-sterically hindered phenyl ligand can be easily transferred to the reaction center, leading to competition between the desired cross-coupling and a phenyl shift. The use of more sterically hindered ligands like tri(o-tolyl)phosphine has been shown to prevent this side reaction. Other side reactions are hydrolytic destannylation by traces of water and/or acid, incorporation of carbon monoxide, resulting in a carbonyl, and reductive debromination.

The competition between the desired coupling reaction and side-reactions is greatly affected by the speed of the reaction and the conditions used. The use of DMF or NMP as the solvent is known to speed up the reaction and the use of these solvents therefore tends to an improvement in selectivity[64]. This also suggests for the use of a more active catalyst systems with more electron rich ligands such as n-heterocyclic carbenes or sterically hindered trialkyl phosphines. There are reports which claim that there is an increase in selectivity using copper(I)salts and fluoride ions, but these results are not easy reproduced[65,66] . Beside the possible side reactions, the toxicity of stannanes is also becoming more of a problem, leading to an increasing interest in the Suzuki coupling.

Suzuki Coupling

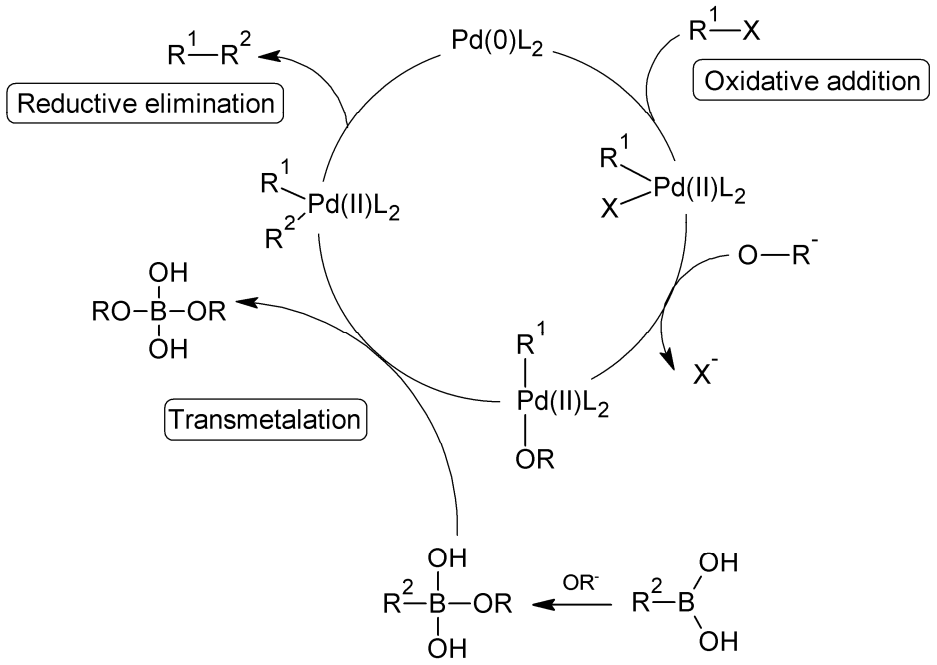


Figure 1.12 Catalytic cycle of the Suzuki cross-coupling reaction.

Very similar to the Stille coupling is the Suzuki coupling. The Suzuki cross-coupling reaction is a palladium catalyzed reaction between organic halide and organoborane compounds. The reaction is suitable for aryl and alkenyl halides and aryl and alkenyl borane compounds. Borane compounds are much less toxic than organostannane compounds. The main difference between the Suzuki mechanism (Figure 1.12) and that of the Stille coupling is that the borane compounds must be activated with, for example, a nucleophile. This activation of the boron atom enhances the polarization of the organic ligand and facilitates transmetalation. The Suzuki cross-coupling reaction can tolerate a wide range of functional groups, similar to the Stille coupling. And although they are not always easy to prepare, boronic derivatives are safer to handle and easy to store.

The side reactions of the Suzuki coupling are comparable with those of the Stille coupling[67]. Homo-coupling, dehalogenation, and phenyl shifts are also occuring in these reactions. Although the major side reaction in the Suzuki coupling is not homo-coupling, but the hydrolytic deboronation, which is facilitated by the presence of the base. The selectivity of the reaction is also strongly affected by pH. Using a stronger base increases the rate of the coupling reaction, but also that of the deboronation and an optimum must be found for each

system. As presented for the Stille coupling the screening for the best reaction conditions is also very important for the Suzuki coupling to achieve high yields.

1.3.4 Determination of the molecular weight of conjugated polymers

GPC[68]

For conjugated polymers it is important to know their molecular weight, for this influences the conjugation length and their ability to self-organize. The most common technique to obtain the molecular weight of polymers is gel permeation chromatography (GPC). The polymer to be analyzed is dissolved and injected into a column containing a porous gel. Molecules with a small hydrodynamic volume get stuck in the small holes in the gel, while molecules with a larger hydrodynamic volume run through more freely. At the end of the column one or more detectors determine when and how much of (concentration) a particular polymer fraction elutes from the column. Several detectors can be used but a UV-VIS detector is commonly used for conjugated polymers. The raw data obtained from GPC is an apparent molecular size distribution, which needs to be converted to true molecular weight distribution using a calibration curve (usually, obtained from polystyrene). This calibration method is a relative calibration, meaning that the molecular weight of the polymers that are analyzed is based on the relative molecular weight of the polymers used for the calibration. If the relationship between hydrodynamic volume and the molecular weight of the analyzed polymers is very different compared to polystyrene, the value obtained can be wrong. More and more research shows[69,70,71] that GPC gives an overestimation of the molecular weight up to a factor four when analyzing conjugated polymers.

MALDI-TOF mass spectrometry (MALDI-TOF MS)[72,73]

Matrix-assisted laser desorption ionisation time of flight mass spectrometry (MALDI-TOF MS) was developed for the analysis of molecules with high molecular weights. The traditional mass spectrometry techniques were limited to the determination of lower molecular masses and could only be used if the sample could be evaporated and ionized. After the 1960s the ionization process was in most cases done by laser radiation, so called Laser Desorption/Ionisation (LDI). In LDI a laser pulse is shot on the sample. The laser light both desorbs and ionizes a sample. The mass of the ions analyzable by this way was, however, limited. Higher masses could not be measured because of destructive ionization,

until in 1987, two groups came up with a solution. Hillenkamp et al[74] and Tanaka et al[72] came up with a solid or liquid matrix, respectively, to control the energy transfer and prevent fragmentation. Molecular masses up to 1500000 could now be measured. The technique developed quickly and has been of great value in the analysis of heavy molecules like proteins and synthetic polymers.

Matrix Assisted LDI or MALDI generates high-mass ions by irradiating a solid or liquid mixture of a sample in a suitable matrix. This irradiation is done with a pulsed uv laser beam. The ratio (w/w) of sample to matrix is low, typically 1:10. Using a matrix prevents the direct ionisation of the sample. The energy of the laser is absorbed by the matrix, which then instantly goes into the gas phase. Every laser pulse ionizes more material and a dense cloud of ionized molecules is formed. The low concentration of the sample prevents direct ionization, which would give extensive fragmentation. It also reduces the formation of clusters and causes less multiple ionizations. After this ionisation process the ions are introduced into the mass spectrometer and analyzed. There are various spectrometers like Fourier transform, magnetic sector, Paul trap, and Quadrupole that can be used, but the most common spectrometer is the TOF or Time of Flight spectrometer. The measurement is based on the difference in acceleration between ions with different masses. The sample ions are accelerated by applying a voltage between two plates in the sample chamber. The ions then drift through the drift chamber and hit a detector at the end. The intensities and flight times of each ion are registered. The time of flight is related to the mass according to Formula 1

$$t = (m/2eUz)^{1/2} L \quad (1)$$

with t = time of flight, m = mass, z = number of charges, U = acceleration voltage and L=drift region. Thus, the time of flight of an ion can be directly converted into its mass by formula (2). This then gives the MALDI-TOF spectrum (see Figure 1.13)

$$m/z = 2eU(t/L)^2 \quad (2)$$

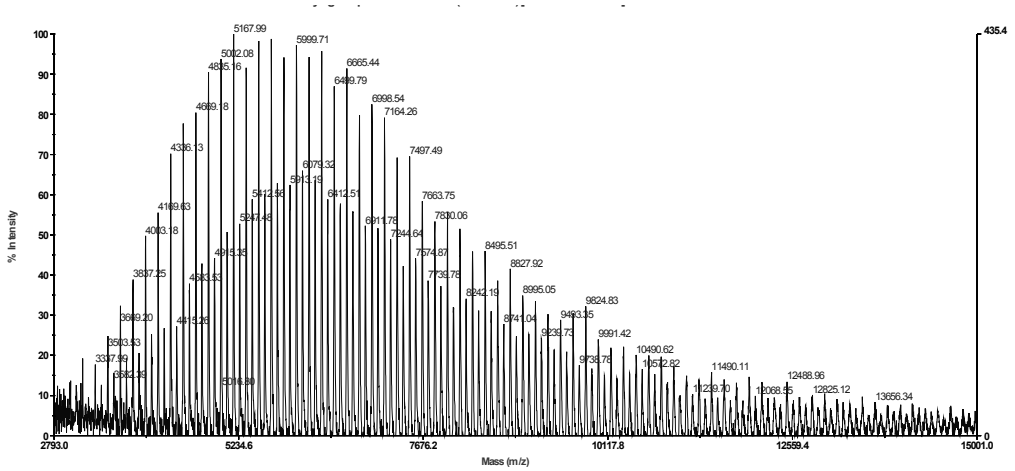


Figure 1.13 MALDI-TOF spectra of RR-P3HT .

The MALDI-TOF MS technique has become a powerful tool for the determination of the molecular weight of conjugated polymers. It is not as common method as GPC, but it is being used much more frequently. The technique MALDI-TOF MS has several big advantages over GPC. One major advantage is the fact that MALDI-TOF MS gives an absolute value for the molecular weight of the polymer — there is no need for calibration to obtain an estimate of the molecular weight. It is also fast, as analysis can be accomplished within a few minutes, and is convenient because submilligram quantities of the material are sufficient for the analysis. MALDI-TOF is also used for the mass-analysis of oligomers. Oligomers, in most cases, have a molecular weight lower than 5000 and are generaly not easily analyzed with GPC (depending on the column used). At low molecular weights calibration can become inaccurate and GPC gives incorrect masses. These polymers can be correctly analyzed with MALDI-TOF MS. Analysis by MALDI-TOF on polymers does not only give the absolute molecular weight of the polymer fractions in the sample, but also structural information like end groups, contamination and the mass of repeating units can be obtained from MALDI-TOF MS[69].

One important disadvantage of MALDI-TOF is the laborious search for suitable ionization conditions, this includes the search for a suitable matrix, other additives (salts) to improve ionization and the correct laser adjustments. Another problem is the difference in sensitivity of the MALDI-TOF MS at different molecular weights of the sample. Small chains fly more easily, leading to a mass discrimination of large polymer chains. Wallace et al. showed[75] that this can be partially overcome by using the low mass gate of the MALDI-TOF machine. But in general, for polymers with a polydispersity larger than 1.2, it is not possible to say

anything about the mass distribution. To analyze polymers with a polydispersity larger than 1.2 one can combine GPC with MALDI-TOF MS. By fractionating the sample using GPC and subsequently analyzing those fractions with MALDI-TOF MS, it is possible to get information about the molecular weight distribution of the complete sample[76].

Although MALDI-TOF MS was developed for the analysis of proteins, more and more synthetic polymers, including conjugated polymers, are also analysed using this technique. However the results obtained from MALDI-TOF MS generate, in many cases, more questions than they answer. This is the reason why MALDI-TOF MS is used very selectively. For polymers made using well defined polymerization methods, the technique is used often and has proven a powerful tool to obtain both structural information as information about the mass of the polymer. For other polymerization methods like oxidative coupling and cross-coupling reactions such as Stille and Suzuki, the MALDI-TOF MS results are often left out. Chapter 6 of this thesis will discuss the reasons.

1.4 Functionalized polymers for the use in (bio)sensors

1.4.1 Introduction

In the previous paragraphs stability, mobility, and the synthesis and characterization of conjugated polymers, (and more specific polythiophenes) was discussed. Major applications of these non-functionalized conjugated polymers can be found in polymer FETs, polymer LEDs and solar cells as previously mentioned. But the conjugated polymers are also extensively studied in the field of organic (bio)sensors. The unique electrical, electrochemical and optical properties of conjugated polymers makes them great candidate materials for converting chemical, biological, and/or physical changes into a electrical-(electrochemical sensor) or optical signals (optical sensor). A brief overview of this field will be given with the focus on the use of functionalized p-type polymers.

The development of new (bio)sensors is a popular research areas at the intersection of biological and engineering sciences. One of the major reasons is the fast growing population, especially in the developing world, and their need for cheaper biosensors that are easier to produce for managing the health care problems. It is believed that combining the extensive knowledge of the semiconductor industry with that of the emerging field of nanotechnology will result in a new generation of biosensors with high sensitivities, small sizes, easy fabrication, and easy read-out.

A sensor is generally built from three functional units[77]; 1) the receptor, which responds to a certain chemical, physical or biochemical change, 2) a transducer which transforms this "detection" into a measurable signal, and 3) the amplifier which increases the intensity of the signal. The most common sensors are conductometric sensors, which display the change in conductivity of a material in response to an analyte, potentiometric sensors which measure a change in potential or charge accumulation, galvanometric sensors which measure a change in current, and colorimetric sensors which measure a change in the materials optical absorption. More sensors are known, and more detailed information can be found elsewhere[78,79].

1.4.2 Functionalized conjugated polymers

It is very important for sensors to have a receptor that is very specific for a certain analyte and this is also the case for sensors based on conjugated polymers. In conjugated polymers specificity can result from covalent or physical integration of receptors, imprinting or the overall electrostatic and chemical characteristic of the conjugated polymer. This thesis will focus only on the use of functionalized conjugated polymers.

Conjugated polymers with pH responsive and redox active groups are, of course, materials which have been studied extensively[80]. From the more complex systems, sensors based on metal ion detection are one of the most studied systems. The results obtained over the years have shown that is possible to make very sensitive and selective metal ion sensors using conjugated polymers[81]. These polymers often contain polyalkyl ether side chains, crown ethers, aza crown ethers or calixarenes for the complexation of alkali metal ions (Na^+, Li^+ or K^+) or bipyridyl-based derivatives for the complexation of other ions like Cu^{2+}, Mn^{2+}, Pd^{2+}, Ba^{2+}, and others. Polymers in several of these systems are given in Figure 1.14. The basic principle behind al of these sensors is that binding of a ion will cause a change in the redox (oxidation & reduction) switching behaviour of the polymer. For example Bäuerle et al. showed[82,83] that polythiophenes synthesised from mono-, bi-, and tert-thiophenes functionalized with pendant 12-crown-4 substituents showed a shift in both their anodic and cathodic current maxima (CV) when Na^+, Li^+ or K^+ ions where added. The largest effect was seen when Li^+ ions where added, which is consistent with the known fact that the 12-crown-4 moiety binds Li^+ the best. In 1995 Bäuerle[84] extended his research by synthesizing a series of polymers with the larger 15-crown-5 and 18-crown-6 ethers attached directly or pendant to a polymer/oligomer backbone. The results they obtained where consistent with the correlation between the ion and macrocycle size.

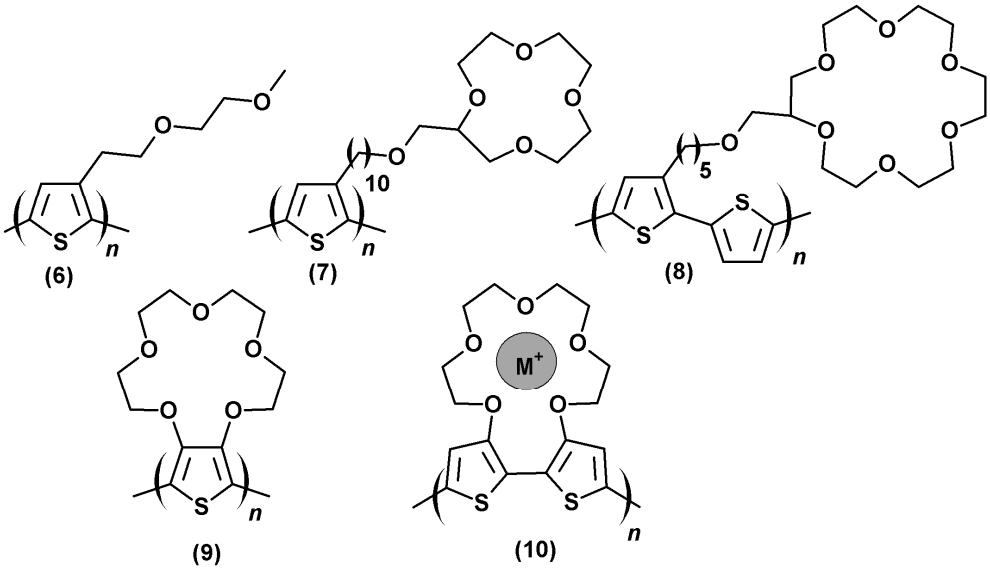


Figure 1.14 Examples of conjugated polymers made for alkali metal ion sensing as found in literature.

The read-out of this sensor can be done using cyclic voltametry and this type of sensor can therefore be considered as a potentiometric sensor. Similar in structure, although different in function, were the sensors from Marsella and Swager[85,86,87,88,89]. They synthesized polymers from a bithiophene unit containing linked oligo oxyethylene ether units. Without alkali ions the polymer would adopt a normal non-twisted structure, but after binding of alkali ions a more twisted structure was obtained. Using this principle a polymer with an ion specific UV-vis response (colorimetric sensor) was obtained. It was also Swager[90] who showed the first molecular recognition-based response. By polymerizing 3,3'-bis(2-methoxyethoxy)-2,2'-bithiophene he obtained a reversible sensor for the (4,4'-dimethylbipyridinium)cation (methyl viologen). The function of the sensor is based on the strong π-π interaction of the viologen molecule and the macrocycle of the conjugated polymer. Using a flow cell device he showed that the conductivity of the polymer decreased upon addition of the viologen. The conductivity changes were ascribed to a charge transfer effect between the donor (conjugated polymer) and acceptor (viologen) of the system. The previous examples are only a small fraction of the systems discussed in literature for the detection of ions or small molecules.

For the fabrication of biosensors it is more important to look at polymers with selective groups which are able to recognize molecules of biological interest. Most of the biosensors in the literature are not based on the covalent attachment of receptor, but on the embedding

of the receptors in the film during the electrochemical polymerization. For delicate systems this is not a suitable method.

The transduction mechanism of the few examples of biosensors with covalently bound receptors is in most cases based on a conformational change in the conjugated polymer upon binding of the protein, cell, or DNA strand. This results in a change in the optical and redox properties of the polymers. Faïd and Leclerc demonstrated[91,92] that biotin functionalized polythiophene can detect the binding of avidin, based on a change in UV-vis absorbance. Higgins et al later extended the research by showing a large decrease and positive shift in the oxidation wave after exposure to avidin using a similar polythiophene system[93]. Other successfully used, covalently linked, receptors are oligonucleotides, nucleobases, bioactive peptides, and functional groups as acids, amines, and maleimides[81,94,95]

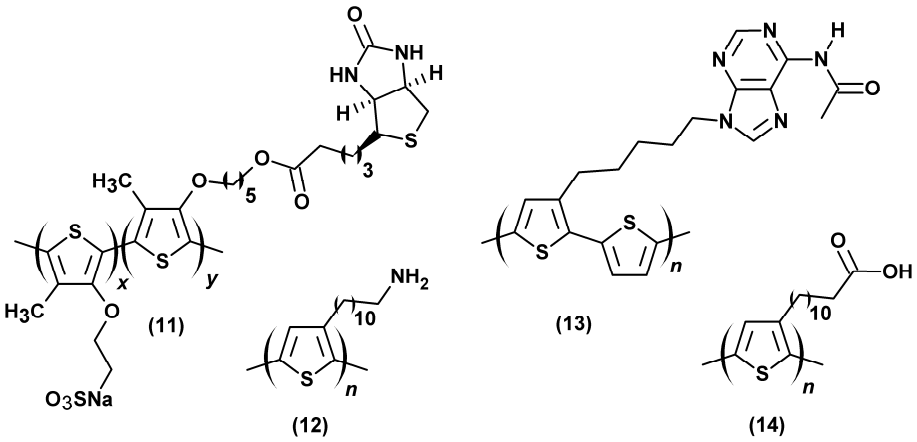


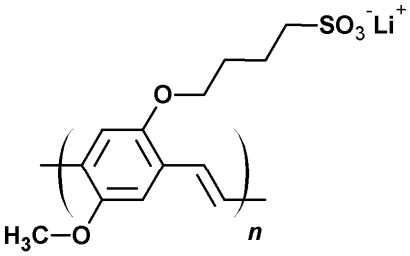
Figure 1.15 Examples of conjugated polymers made for sensing bioactive compounds, as found in literature.

The effect of the binding of the analyte is in most cases minimal, resulting in only a small change in electronic properties of the conjugated polymer. This makes electrochemical detection difficult.

A more promising technique was shown by Chen et al. who synthesized sulfonate functionalized polyphenylene vinylene and found that the complexation of methyl viologen by electrostatic interaction caused complete quenching of the fluorescence of the polymer[96] The quenching was six orders of magnitude more effective than that of a diluted stilbene solution. Chen calculated that one metal viologen molecule per polymer chain was enough to quench the fluorescence of the complete system. He then synthesized a methyl viologen coupled with a biotin unit and showed that addition of this molecule also quenched the fluorescence successfully. By applying the complementary avidin the fluorescence was

restored resulting from the selective binding of the biotin with the avidin and diffusion from the surface of the polymer. Very low concentrations (1.2×10^{-8} M) of avidin resulted in a complete recovery of the fluorescence proving that it is very sensitive technique. The main mechanism proposed by Chen was that of intermolecular electron transfer between the donor (polymer) and acceptor (MV) molecules. But the quenching mechanism might be more complicated and arise also from efficient internal energy transfer and long-range resonance energy transfer (FRET)[97].

This enhanced fluorescence quenching was adopted for other systems and used in the detection of enzyme cleaving, binding of other enzymes, or antigens but most important DNA detection[98,99,100,101,102,103,104]. The negativly charged phosphate groups of single stranded DNA can undergo electrostatic interaction with the positively charged functional groups of a conjugated polymer. When a chromophore, coupled with a complementary sDNA or polynuclease strand, binds to the DNA, energy transfer occurs, and the fluorescence of the polymer is quenched and in most cases it enhances the fluorescence of the chromophore. A lot of effort has been put into the improvement of this system because of its high commercial potential. Conjugated polymers used in these biosensors are homo-polymers or co-polymers based on poly(phenylene vinylene)s and poly(fluorene)s. The functional groups are sulfonate or N,N,N-trimethyl ammonium ions.



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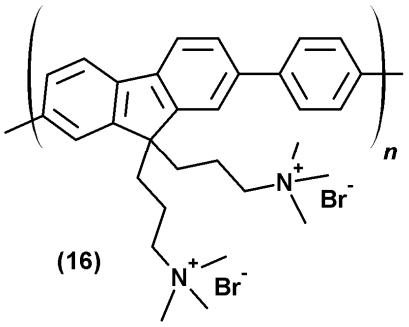

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Figure 1.16 Common conjugated polymers used in literature for (bio)sensing using enhanced fluorenscence.

1.5 Aim and outline of this thesis

The research described in this thesis is part of larger project called the BioFET program. The aim of this project is to develop a new type of micro biosensor based on an organic field effect transistor. The project crosses the boundaries of many fields and is therefore performed in close collaboration with the device physics group op Prof. Paul Blom and the biochemistry group of Prof. Bert Poolman within our institute. Our goal is to develop a conjugated polymer with high stability under ambient conditions, a high mobility in the field effect transistor, and which can be easily functionalization with a protein receptor.

As described in the previous chapters, the combination of a polymer that shows a high stability towards oxidation by oxygen and water and a high mobility is not trivial. A polymer is needed with a high oxidation potential and a very regular structure to obtain highly ordered semicrystalline films with high conductivity. McCulloch showed that co-polymerization of alkyl functionalized bithiophenes with the cross-conjugated thieno[2,3-b]thiophene resulted in a polymer with a very high mobility and stability under ambient conditions.

In Chapter 2, the synthesis of this reference polymer and several of its thienothiophene derivatives will be discussed. The synthesis of both the alkyl functionalized bithiophene monomers and that of thieno[2,3-b]thiophene were optimized before the synthetic routes could be applied to the synthesis of the functionalized polymers.

In Chapter 3 we adapt a synthetic route for alkyl functionalized bithiophene monomers for the synthesis of several functionalized bithiophene monomers. Challenging synthetic problems will be discussed, including deprotection using BBr_3 and functionalization with the desired maleimide. In this chapter we will also discuss the choice of maleimide as our functional group and a short overview of the results of our collaborators on the synthesis on the protein receptor will be given for better understanding.

Chapter 4 describes the results of the polymerization of our functionalized bithiophene units with thieno[2,3-b]thiophene and the problems encountered. Possible intra-molecular charge transfer between the maleimide and the conjugated polymer led to the need for another Michael acceptor. The post functionalization of the bromide functionalized polymer with an acrylate acceptor will be discussed. The functionalization, which revealed a flaw in the polymerization process, was characterized by MALDI-TOF MS.

More detailed analysis using MALDI-TOF MS on the Stille-coupling products are discussed in Chapter 5 and it is pointed out more clearly that Stille-couplings are not suitable for the synthesis of high molecular weight conjugated polymers with a regular structure.

In Chapter 6 the use of bis(pinacolato)diborane as coupling reagent in a homopolymerization is presented and is shown to be a successful polymerization method for bithiophenes, terthiophenes, quarterthiophenes, and fluorenes. The method is compared to other homo-coupling methods. In the second part of this Chapter the use of this new method for the synthesis of the functionalized conjugated polymers will be discussed.

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